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Visualization of nanodiamond formation in molten carbon under pressure

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Abstract

We discuss the characteristics and visualization of simulations of nanodiamond clusters grown from molten carbon. The general trends of nanodiamond size and quality as functions of growth conditions resemble those found experimentally. In particular, the probability of finding nanodiamonds, and their quality increased with increasing sample density and cooling rate. We also discuss finite size effects and possible phase transitions within molten graphite.

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1. Introduction

Carbon poses a special challenge to simulation and visualization because the different hybridizations lead to different numbers of neighbours and geometric structures. There may be two (e.g. linear chains or carbyne phase), three, when the bonding is known as sp^2 (e.g. graphite) and four, known as sp^3 (e.g. diamond). Distinguishing visually between these types of bonding of atoms and the corresponding structures was one of the main motivations behind the Computational Physics Group at the Technion's development of our own visualization code. This code is called AViz, short for Atomistic VIZualization.

If carbon only took the two forms of diamond and graphite, that would be enough to make it special. However, as well as carbon being one of the building blocks of organic molecules, pure carbon can take the form of buckyballs, nanotubes etc. And if that were not sufficient, in addition to hexagonal diamond, there is another, cubic, solid known as lonsdaleite, whose distinction from the cubic form is very difficult, making most other carbon simulation visualization issues [1] appear trivial.

In the carbon phase diagram, graphite is the stable form at atmospheric pressure. Diamond formation and stability require higher pressures. Natural diamonds were formed deep within

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the earth; between 100 km and 200 km below the surface, at temperatures of 900 - 1300 C and pressures of 45 - 60 kilobars, then carried to the surface by volcanic eruptions. To ensure they are not converted to graphite en route, their transport must be extremely rapid. Diamonds can also form in meteorites and have been created artificially. One group of artificial preparations mimics nature, requiring both high pressures and temperatures. It is also possible to grow carbon films in the laboratory with Chemical Vapour Deposition, (CVD) under conditions very different to those expected from the C equilibrium phase diagram. When special gas composition and pressure conditions are invoked, nanodiamonds embedded in an amorphous carbon matrix will form. Thus relevant parameters are temperature, pressure and the nature of the carbon matrix surrounding the incipient diamond crystallites.

2. Growing computer nanodiamond

Diamond has a high melting point and the temperatures nature requires to prepare diamond are even higher. In addition, there is a curious finite size scaling effect that leads us to require even higher temperatures for small simulation samples. Rosenblum et al [2] first suspected interesting scaling for finite carbon samples during the modeling of thermal stress at a diamond surface. They found that artificially adjusting the “mismatch factor” gave the same effect as increasing sample size. Sorkin et al [3] found that the smaller the sample, the larger the temperature needs to be for equivalent behaviour, and demonstrated a universal collapse of scaling to confirm this. Since temperature on an atomistic scale is just kinetic energy smaller samples just seem to need more energy to make their moves.

We explored the simulation of nanodiamond growth with or without hydrogen in two recent papers [3, 4]. Growing nanodiamonds is just as tricky on the computer as in nature. It is not as simple as generating a small bit of carbon with atoms at the diamond lattice spacing because if a diamond surface is not covered with something to hold in the local pressure, the diamond will simply relax into graphite, [6]. A common solution has been the termination of external surfaces with hydrogen atoms. However in one study of nanodiamond terminated with H atoms, the claimed properties of quantum confinement were later shown to be nothing more than a consequence of the surrounding hydrogen atoms.

We can get a clue from the CVD samples used by our experimental partners which contain small diamond crystallites enclosed in an amorphous C matrix. Amorphous carbon surrounds have far less influence on the characteristics of the nanodiamonds than does termination by atoms of other elements. However building a diamond sample and then artificially sticking amorphous C around it would require further equilibration, during which changes may occur within the nanodiamond seed. This is certainly not a practical scheme for sample development. Therefore, in order to generate nanodiamonds we went the long route of mimicking nature by melting and subsequent rapid cooling of the carbon sample. We varied external pressure, direction of the pressure, relaxation times, and hydrogen content to determine the optimal computer conditions for nanodiamond formation.

In order to compare the computer generated nanodiamond with real nanodiamond we must calculate the density of states (DOS) and band gaps as well as make measurements of its structural properties. Both for these calculations and during the sample preparation we need to observe real dynamics, hence tight-binding molecular dynamics is suited; we used the OXON code [7].

The samples were initially arranged as a perfect diamond crystal of size $3 \times 3 \times 3$ unit cells (i.e. 216 carbon atoms) with a density of 3.3 g/cc. They were melted at a temperature of 8000 K during 5, 10, 15, 20 and 25 ps. These times are sufficient to ensure the liquid phase

reached equilibrium. Thus we generated five different liquid carbon samples. In order to generate amorphous carbon networks with different densities each of the five liquid configurations were isotropically compressed by changing the volume of the unit cell to 3.3, 3.5, 3.7, 3.9 and 4.1 g/cc. Pressures at 8000 K for the densities of 3.3, 3.5, 3.7, 3.9 and 4.1 g/cc correspond to 60, 80, 110, 140, 250 GPa respectively.

The compression was followed by a rapid cooling to 300 K with cooling rates of 500 K/ps, 25 simulations in all. In order to simulate an expansion, samples at 3.7, 3.9 and 4.1 were then homogeneously expanded to reduce the density to the natural diamond value of 3.5 g/cc. Then the samples were “annealed” by repeatedly heating to 1000 K and then cooling to 300 K during 10 ps. This cooling time is physically realistic and provides a range of conditions within a real “thermal spike”, as generated when energetic C atoms slow down in matter. As a result of this repeated “annealing” cycle only a few atoms slightly changed their position or their hybridization (for example in the sample of 3.9 g/cc the percentage of the sp coordinated atoms changed from 88 to 86). Some samples had between 2 and 25 hydrogen atoms inserted after the initial development but before the “annealing” stage.

3. Results and discussion

In many cases we found nanodiamond crystallites embedded within our amorphous C. The Density of States (DOS) of one of them is shown in figure 1. Our “success rate” of obtaining nanodiamond crystallites is higher than those in the few previous calculations made for limited cases without hydrogen. It is the only success with hydrogen. We are not sure if this is due to more care in the preparation, better statistics or simply our use of AViz to identify the nanodiamonds.

Once the samples were prepared, we carried out different measurements, including sizes of sp^3 clusters, of nanodiamonds, percentage of sp^2/sp^3 , radial and angular distributions, DOS and band gaps. In cases where nanodiamonds failed to form, amorphous sp^3 networks, graphitic planes or mixtures of the above were found. Statistics of repeated cases with different seeds and consistent trends support the conclusions that the probability to find crystallites increases with density and with cooling rate. This is in agreement with laboratory experiment. The details of the results can be found in [4] and [5].

Finally, we wish to discuss some additional, tantalising features for which we do not yet have sufficient statistics to make definitive claims. In some sizes and cases we observed a phase transition within the intermediate liquid carbon phase, as shown in figure 2. Such a structural first order phase transition in liquid carbon was experimentally suggested by M. Togaya [8] and later predicted by Glosly and Ree [9] in their calculations with the Brenner bond-order potential. This phase transition is characterized by a sudden transition from sp^2 -coordinated to sp^3 -coordinated carbon in the liquid phase at a pressure of 5-15 GPa and a temperature of about 6000-9000 K.

Recently, Wang et al [10] carried out ab initio calculations of the carbon phase diagram, and did not find evidence for a first order liquid-liquid phase transition in their conditions. Morris et al [11] simulated liquid carbon at 6000 K in a wide range of densities (1.5-4.2 g/cc). They did not observe graphitization during 700 fs. The above reports show that this transition in liquid carbon is controversial to say the least. Our simulations last up to 60 ps, longer than those of the others. We found that at a temperature range of 5000-7000 K the probability of the phase transition is not large (one out of 5, two week simulations). However, we feel that a comprehensive investigation could shed further light on this issue, even if the state is metastable. After all diamond itself is not the carbon groundstate.

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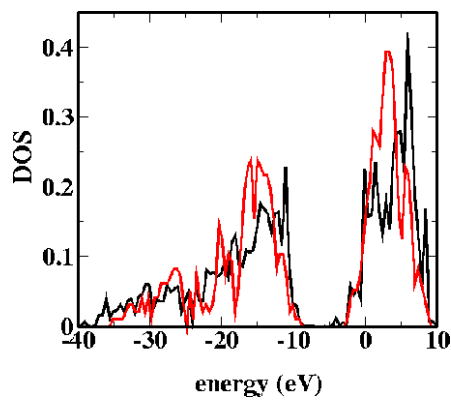


Figure 1: Density of state of diamond cluster grown up within an amorphous carbon network (black line) compared to that of perfect diamond (red line)

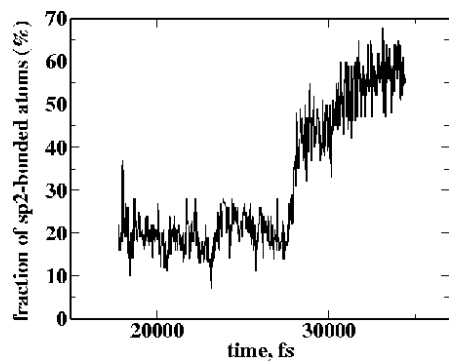


Figure 2: Graph of the percentage of sp^2 -coordinated atoms in liquid carbon at 3.9 g/cc and 6000 K as a function of time.